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Conversation of Dissolved Manganese to Particulate Manganese During Diatom Bloom Effects on the Manganese Cycle in the MERL Microcosms

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Conversion of Dissolved Manganese to Particulate Manganese During Diatom Bloom: Effects on the Manganese Cycle in the MERL Microcosms

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ABSTRACT

Conversion of dissolved manganese to particulate manganese occurred during a minor diatom bloom during August and September 1978 in the MERL microcosms. Correlations between chlorophyll a and particulate manganese suggest that 29 moles Mn were transferred to the particulate phase for every mole of chlorophyll formed during the active growth of the diatoms. The particulate manganese formed was primarily removed to the sediments after the bloom terminated. Budgetary considerations indicate that the major input (90 to 95%) of manganese to the water column of the MERL tanks during the warm seasons is from benthic remobilization. Total manganese concentrations, observed on a weekly basis, suggest that the tanks are in steady state with this benthic input. A rapid return flux of manganese to the sediments must occur to maintain this steady state. Removal of manganese from the water column during the growth of diatoms could account for no more than 7% of the average daily benthic flux during the August-to-September period. The exact mechanism(s) involved in balancing the benthic flux have not been fully isolated. However, the ability to sample large, controlled ecosystems repeatedly over short time scales provides a system in which the geochemical cycle of manganese (plus other elements) can be readily modeled.

Manganese is one of the most chemically reactive metals in aquatic systems. Manganese speciation depends on a variety of factors, of which pH and redox conditions are the most important (Stumm and Morgan, 1970). Manganese is also important biologically as an essential metal nutrient (O'Kelley, 1973). The combination of chemical and biological reactivity causes manganese to have complicated geochemical cycles, particularly in estuaries, where a variety of

redox conditions can exist and variable yet intense biological activity is present. Additionally, tidal mixing in estuaries can act to dilute and redistribute the freshwater manganese flux to the estuary.

Conservative behavior for total manganese in estuaries has been reported by Graham, Bender, and Klinkhammer (1976) and, for dissolved manganese, by Holiday and Liss (1976). Nonconservative behavior of dissolved manganese was observed by Evans et al. (1977), Sanders (1978), and Graham, Bender, and Klinkhammer (1976). Nonconservative behavior of dissolved manganese is often attributed to the benthic flux of manganese into the water column.

Removal of dissolved ^{54}Mn from the water column of controlled marine ecosystems occurs with half-lives on the order of 2 to 14 days (Santschi, Li, and Carson, 1980). In these same systems diffusion of ^{54}Mn from sediments balances the removal within 11 to 25 days, resulting in steady-state conditions over very short time scales. Turekian (1977) suggested that the dominant feature in the manganese cycle within estuaries is the benthic flux of dissolved manganese, which is rapidly converted to particulate forms [$t_{1/2} \approx 2$ days (Graham, Bender, and Klinkhammer, 1976)] and redeposited. The form of the particulate matter involved in the depositional process has not been well characterized, however. Cycling of manganese between sediments and water, and vice versa, is apparent from these studies and occurs over short time scales.

The concentration of total manganese in the water column of an estuary may be influenced by the relative rate of physical mixing vs. the conversion rate of dissolved to particulate manganese and also the time required for deposition of this particulate phase. In other words, if mixing is slower than the return flux, the benthic flux will be the dominant mechanism affecting manganese concentrations within the water column. On the other hand, if the mixing rate is rapid compared with the return flux, the dominant process that establishes manganese concentrations within an estuary will be the mixing rate. Santschi, Li, and Çarson (1980) suggested that the balance between these rates may lead to an apparent conservative behavior of manganese in estuaries.

Additional modification of dissolved, particulate, and total manganese concentrations may result from incorporation of manganese into actively growing phytoplankton (Morris, 1971). The role, if any, of this biological phase transition in the estuarine cycle of manganese is not readily apparent.

We report here that dissolved manganese can be transformed to the particulate state during growth of certain diatoms in controlled marine ecosystems and by extension in natural marine waters.

Sedimentation of manganese in association with these biologically derived solids appears to provide a potential mechanism for removing manganese from the water column to sediments.

EXPERIMENT

The Experimental Facility

This study was conducted in the Marine Ecosystems Research Laboratory (MERL). The MERL microcosms were described by Pilson et al. (1977) and Pilson, Oviatt, and Nixon (this volume). Adler, Amdurer, and Santschi (this volume) supply further information on the operation of the tanks during the period covered by this paper. Briefly, the MERL system consists of 12 cylindrical tanks (5.5 by 1.5 m) filled with 13 m^3 of seawater, which overlies 30 cm of sediments with a surface area of 2.5 m^2. Seawater is supplied to the tanks from the lower west passage of Narragansett Bay in four daily pulse feed cycles of 120 liters each. This provides a turnover time of ~30 days ($t_{½}$ = 19 days). Tank mixing is provided by a plunger-like device that operates for two consecutive hours out of every six. Nine tanks are treated in groups of three in stressing experiments. The remaining three tanks are used for radiotracer experiments.

The data discussed in this paper were obtained between July 25 and Sept. 19, 1978. Previously the tanks used in stressing experiments were observed for 7 weeks (Jan. 17 to Mar. 6, 1978) to establish the initial replicability between tanks. Between Mar. 6 and July 6, 1978, the water-accommodated fraction of No. 2 fuel oil was added to tanks 2, 7, and 9 at an average concentration of 93 μg/liter. Tanks 1, 5, and 8 were maintained as controls, and 3, 4, and 6 were used for a variety of biological experiments. After July 6 the oil-treated tanks were allowed to function without further oil addition. Thus no oil was added to tanks 2, 7, and 9 in the 26 days before the period discussed here. Petroleum hydrocarbons in the water column of the oil-stressed tanks had decreased to typical background levels (<10 μg/liter as total hydrocarbons) by mid-August. Over the course of the oil additions, ~45% of the saturated and 10% of the aromatic hydrocarbons added to the tanks were found in the upper 3 cm of the sediment column (Gearing and Gearing, 1978).

Suspended loads in the control tanks attained values of 8 to 12 mg/liter during the spring, whereas suspended loads in the oil-stressed tanks were consistently between 2 and 4 mg/liter. Our preliminary results suggest that, on a per-unit-weight basis, suspended

matter in the oil-stressed tanks contained significantly less aluminum than did the control tanks. These results suggest that there was a lower fraction of lithogenous material in the oil-stressed tanks than in the control tanks before our experiment. The preliminary suggestion from this data is that less resuspension of bottom sediments occurred in the oil-stressed tanks. Furthermore, the suspended loads in all tanks decreased to < 3 mg/liter at some point during the 30 days before July 25. As a result, the concentration of suspended matter in the tanks during the early weeks of the period discussed here was consistently low.

The data presented here contrast an oil-stressed tank (tank 2) and a control tank (tank 8), which showed distinctly different manganese responses from early August to mid-September 1978. Additional supporting data from tanks 3, 4, and 7 are discussed as necessary. The conclusions reached cannot be clearly ascribed to the oil-stressing experiment although some, as yet undetermined, effects may be present.

Analytical Methods

Tank samples (500 ml) were collected weekly on Tuesday morning at 0930 (1 hr into a mixing cycle) from 10 cm below the tank surface. Previous replicability experiments have shown that dissolved metals, particulate manganese, and suspended loads are homogenous after 1 hr of mixing. A 5-ml aliquot of water was taken from the tank sample, acidified to 1% (vol/vol) with Merck Suprapure HNO_3, and used to estimate total acid-leachable manganese (dissolved plus that readily removed from solid phases) in the tank. The remaining sample volume was then vacuum filtered through preweighed 0.4-μm Nuclepore filters under 10 to 15 psi. The filter was air dried, reweighed, and stored frozen for determination of total suspended solids and particulate metals. One milliliter of the filtrate was acidified, as described, to obtain total dissolved manganese. The remaining filtrate was extracted for other dissolved metals. A pooled water-column sample (equal volumes from three depths) was collected during the same mixing cycle for chlorophyll a, total pigment, nutrients, salinity, and phytoplankton cell counts.

Feedwater to the tanks was sampled in two ways. A sample collection device was placed in the feed line, and water was collected during each feed cycle over a weekly period. This sample gave an integrated input of total acid-leachable manganese to the tanks. Also, a weekly 500-ml water sample was obtained from the feed system and processed as described. This sample served as a check on the results from the integrated sample and also gave an estimate of the

contribution of dissolved manganese to total manganese concentrations in the feedwater.

The benthic flux of dissolved manganese to each tank was determined monthly. The flux was obtained by capping the entire 2.5 m^2 of sediment with a specially designed benthic flux chamber. Initial and final samples were collected in a 50-ml plastic syringe, filtered through 0.4-μm Nuclepore filters, acidified, and analyzed as described.

Láboratory ware (conventional polyethylene when possible), filters, and high-purity water used in the laboratory were prepared according to the procedures outlined by Patterson and Settle (1976). Discrete water samples were collected by holding a capped, clean bottle under the tank surface with plastic-gloved hands, then uncapping and recapping the bottle under water. After transfer to the trace-metal laboratory, samples were processed in Class 100 laminar-flow clean benches. Samples for manganese analysis were generally ready for analysis within 30 min after collection.

All manganese data were obtained by direct analysis of 20 μl of sample with an HGA-2100 graphite furnace interfaced to a Perkin-Elmer model 603 atomic absorption spectrophotometer equipped with a D_2 continuous discharge lamp. Manufacturer's recommended instrument parameters were used. Furnace parameters were: dry at 100°C for 20 sec, char at 900°C for 10 sec, and atomize at 2550°C for 5 sec. Sample concentrations were determined by comparison with standard curves prepared from extracted (Chelex-100, Bio-Rad Laboratories) Narragansett Bay water acidified to 1% (vol/vol) with HNO_3. Detection limits of 10 n*M* and a 4% error as the coefficient of variation at 50 n*M* were determined. The error associated with all flux calculations was estimated to be $\leq$10%.

The analytical procedure described gives information on total manganese, dissolved manganese, and by difference manganese associated with particles greater than 0.4 μm in size. The total acid-leachable manganese fraction includes the dissolved manganese (<0.4 μm) plus that which is solubilized from particulates. This may include manganese adsorbed onto or coating these particulates plus any released from the cells of organisms. This fraction does not include the relatively unreactive manganese associated with lattice positions in lithogenous particles. Dissolved manganese may include colloidal manganese that passes the 0.4-μm pores of the filter as well as truly dissolved manganese. Total pigments (Σp), determined by the fluorometric method of Holm-Hansen et al. (1965), were obtained by summing the chlorophyll a and phaeopigment concentrations. Concentrations of all manganese fractions, chlorophyll a, and Σp are reported on a molar basis.

RESULTS

Time Response of Manganese

On July 25 particulate manganese constituted ~40% of the total manganese in tanks 2 and 8 [Figs. 1(c) and 2(c)]. During the next week the contribution of particulate manganese decreased to < 7% of the total manganese. The particulate phase apparently was removed from the water column to the sediments since tank flushing cannot account for the loss of particulate manganese during this 7-day period. As a result, the total manganese concentrations in both tanks on Aug. 1 were similar (~200 n*M*) and primarily in dissolved form.

After Aug. 1 the particulate and dissolved manganese concentrations in these two tanks did not display similar trends through time. Concentrations of both dissolved and total acid-leachable manganese in tank 2 declined continuously until Aug. 29 [Fig. 1(d)]. After Aug. 29, the total manganese concentration continued to decline, whereas the dissolved manganese concentration increased. By Sept. 19, the two fractions had converged at a total manganese concentration that was 50% of the total manganese concentration on Aug. 1. During this same period neither total acid-leachable nor dissolved manganese concentrations declined in tank 8 [Fig. 2(d)]. Particulate manganese contributed less than 5% to the total manganese concentration [Fig. 2(c)] in tank 8 during this period.

The decline in dissolved manganese in tank 2 was more rapid than the decline in total acid-leachable manganese; this indicates that a phase transition occurred during the same period in which the total manganese concentrations declined in the water column. This conversion is represented in Fig. 1(c), where the percentage of the total manganese found in the dissolved state is plotted against sample date. The contribution of dissolved manganese to total manganese concentration decreased from 94% on Aug. 1 to 8% on Aug. 29 and then increased to 92% on Sept. 19.

The large increase in total manganese on Aug. 29 in both tanks was caused by a wind and rain storm that passed Narragansett Bay the previous day. Generally, heavy rain and wind result in elevated manganese concentrations in Narragansett Bay input water from freshwater runoff and possibly sediment resuspension. This injection of manganese into the tanks was not evident in either tank 1 week later.

Time Response of Phytoplankton

The contrast in phytoplankton biomass between tanks 2 and 8 during the period from July 25 through Sept. 19 was marked. Total

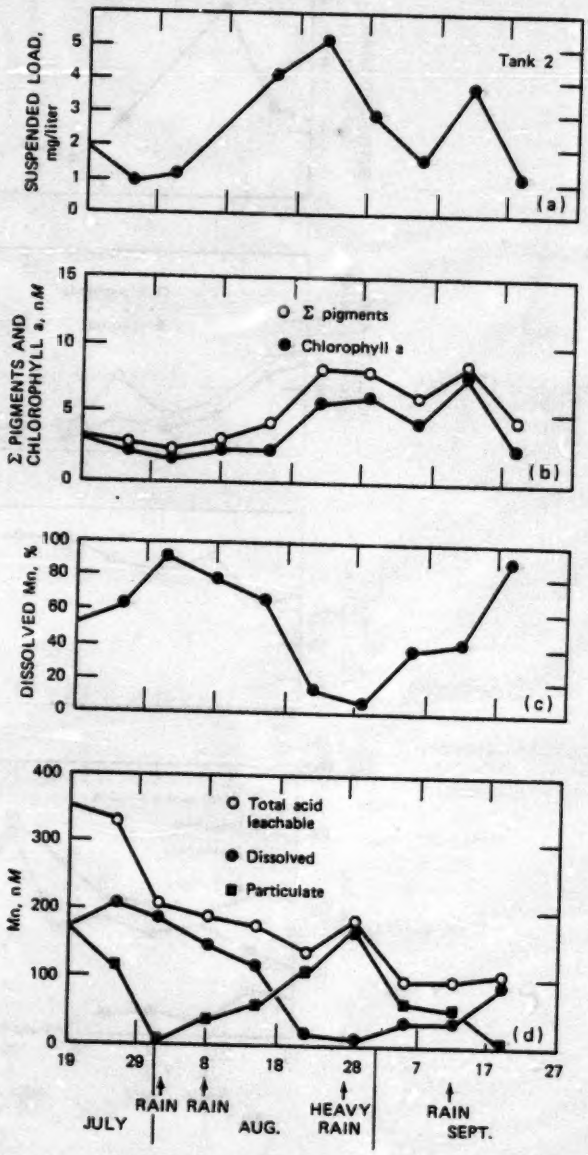

Fig. 1 Suspended load (a); chlorophyll a and total pigments (b); percent dissolved manganese (c); and dissolved, total, and particulate manganese concentrations (d) vs. sample day from MERL tank 2 between July 25 and Sept. 19, 1978.

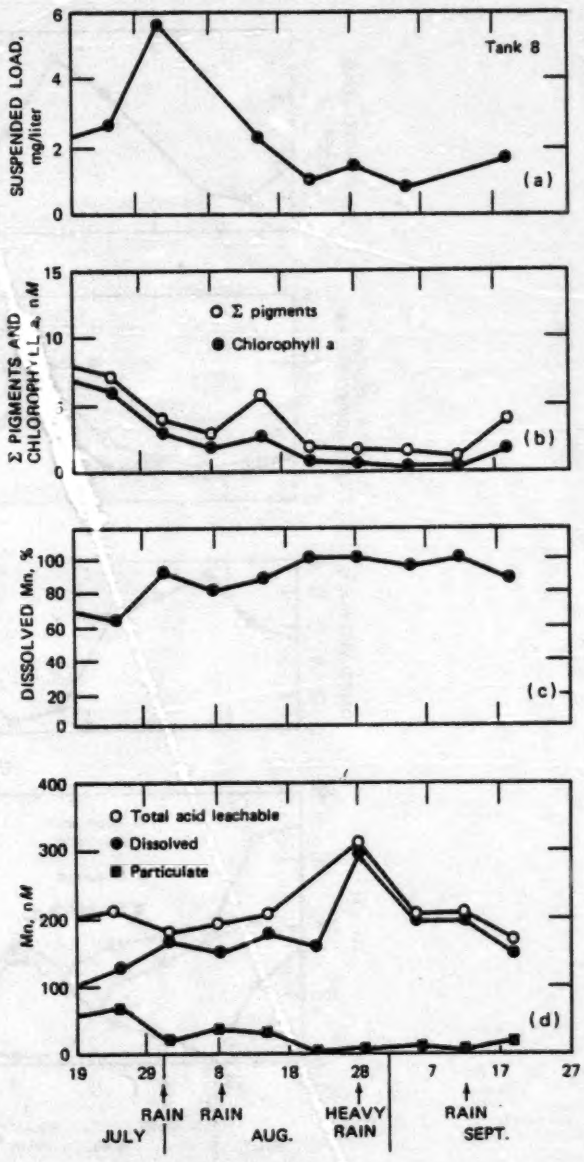

Fig. 2 Suspended load (a); chlorophyll a and total pigments (b); percent dissolved manganese (c); and dissolved, total, and particulate manganese concentrations (d) vs. sample day from MER[illegible]nk 8 between July 25 and Sept. 19, 1978.

pigments and chlorophyll a followed an inverse cycle in both tanks, tank 2 increasing and tank 8 decreasing [Figs. 1(b) and 2(b)]. The community structure also differed dramatically. Diatoms, primarily *Nitzschia pungens* and *Chaetoceros* sp., increased in abundance from Aug. 9 through Sept. 12 (from 85 to 480 live cells/ml) in tank 2 (Table 1). In tank 8, which initially supported a diatom flora dominated by *Leptocylindrus danicus* (4200 live cells/ml on July 25), diatoms declined steadily in abundance and were not a significant component of the phytoplankton community after Aug. 21 (0 live cells/ml). Microflagellates were numerically dominant in both tanks throughout this period (Vargo, 1978). Their seasonal pattern of abundance and total cell concentration was similar in both tanks (1700 and 1100 cells/ml in tanks 2 and 8, respectively). The differences in chlorophyll a and total pigments between tanks 2 and 8 reflect the differences in diatom abundance. These chlorophyll concentrations were not atypical for lower Narragansett Bay in the late summer.

Relationships Between Particulate Manganese and Plant Pigments

On July 25 high particulate manganese concentrations in relation to chlorophyll a were observed in tank 2 (Figs. 3 and 4). Between July 25 and Aug. 1, particulate manganese declined; this indicates removal of the particulate phase bearing the manganese from the tank water column. That the chlorophyll and Σp concentrations did not change suggests that the particulate phase carrying the manganese was not directly related to chlorophyll a nor to Σp at this time. From Aug. 1 to Aug. 29, chlorophyll and Σp increased linearly with particulate manganese ($r = 0.95$ and 0.93, respectively). This period corresponds to the maximum growth of the diatoms as indicated by the chlorophyll concentrations [Fig. 1(b)]. After Aug. 29, the chlorophyll a, Σp, and particulate manganese concentrations declined, with particulate manganese declining more rapidly in relation to the pigments (Sept. 5—19, Figs. 3 and 4). The correspondence between the increase in chlorophyll a, decrease in dissolved manganese, and increase in particulate manganese during the first 5 weeks of diatom growth indicates that conversion of dissolved manganese to particulate manganese was mediated by the diatoms.

Linear regression analysis indicates that the molar ratio of manganese to chlorophyll a and Σp was 29 and 22, respectively (Figs. 3 and 4). Release of manganese from nonliving plankton was not apparent. The linear relationship between Σp and particulate manganese (Fig. 4) suggests that the manganese continued to associate with the plankton even after the organism died. This is also

TABLE 1

SUMMARY OF PHYTOPLANKTON PRESENT IN MERL TANKS FROM JULY 25 TO SEPT. 19, 1978, AND THEIR EFFECTS ON DISSOLVED MANGANESE CONCENTRATIONS

Tank number and species present	Presence of diatoms, weeks	Maximum change in dissolved manganese, n*M*	Maximum total pigment concentration, n*M*	Average total pigment concentration, n*M*
2 Microflagellates *Chaetoceros* sp. *Chaetoceros curvisetum* *Nitzschia pungens*	7	−160	8.1	5.2 ± 2.7
8 Microflagellates	0	+15	0.8	3.0 ± 2.2
3 Microflagellates *Bacillaria paradoxa* *Lithodesmium undulatum*	3–4	−145	8.3	4.6 ± 2.2
4 Microflagellates *Chaetoceros* sp. *Chaetoceros curvisetum*	7	−160	20.2	6.8 ± 5.3
7 Microflagellates *Chaetoceros* sp. *Nitzschia longissima* *Chaetoceros curvisetum* *Lithodesmium undulatum*	3–4	−75	14.2	4.8 ± 4.4

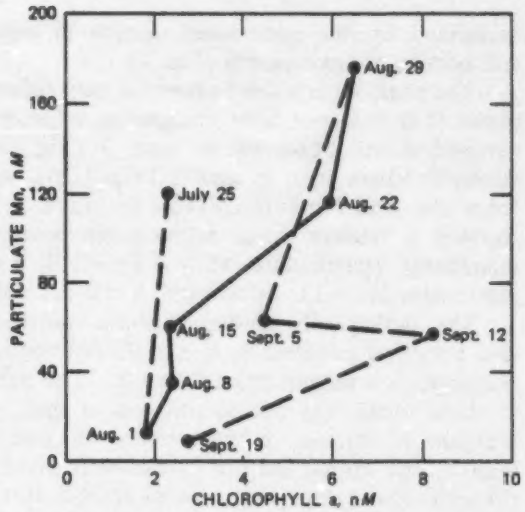

Fig. 3 Particulate manganese vs. chlorophyll a from MERL tank 2 between July 25 and Sept. 19, 1978, weekly sequence of samples. Particulate manganese = 29 chlorophyll a − 29, r = 0.95 (Aug. 1—29).

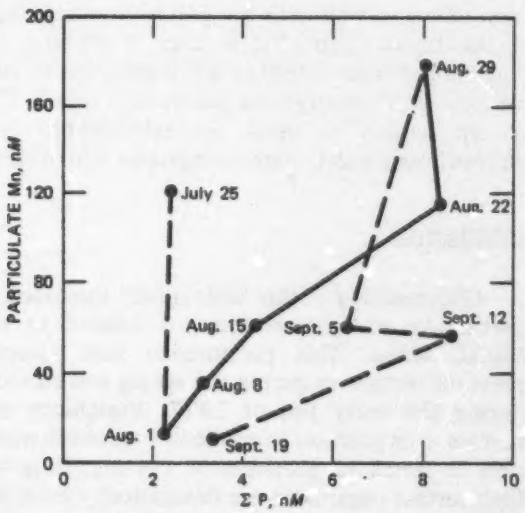

Fig. 4 Particulate manganese vs. total pigments from MERL tank 2, weekly sequence of samples. Particulate manganese = 22 Σp − 35, r = 0.93 (Aug. 1—29).

evidenced by the concurrent decline in pigments, suspended load, and particulate manganese (Fig. 1).

The negative intercept observed may reflect a chlorophyll-bearing phase that does not have manganese associated with it. Chlorophyll concentrations observed in tank 8 [Fig. 2(b)] at this time were generally lower than in tank 2 [Fig. 1(b)], and diatoms were absent from the water column (Table 1). Tank 8, in contrast to tank 2, showed a weaker linear relationship between Σp and particulate manganese (particulate Mn = 5 Σp + 1.6, r = 0.63, and n = 8 and particulate Mn = 11 chlorophyll a − 0.5, r = 0.77, and n = 8.

The biologically mediated phase transition reported for tank 2 also occurred in tanks 3, 4, and 7. The molar ratio of manganese to chlorophyll a ranged from 28 to 37. The particulate transformation in these tanks was not as obvious as that in tank 2, however. The increase in biomass in these tanks was not concurrent with that in tank 2, but similar diatom species were involved (Table 1). The same *Chaetoceros* species that was in tank 2 also grew in tanks 4 and 7, along with *Chaetoceros curvisetum*. Neither species grew in tank 3, but two other large diatoms, *Bacillaria paradoxa* and *Lithodesmium undulatum*, contributed significantly to the total phytoplankton biomass in this tank.

The maximum change in dissolved manganese and maximum Σp corresponded well with the period in which the diatoms were present in the tanks (Table 2). A large short-term (<2 weeks) increase in flagellates (from ~1000 to 4500 cells/ml) in tanks 4 and 7 caused the maximum concentrations shown in Table 2. This short-term increase in Σp tended to mask the relationship between chlorophyll a, diatoms, and particulate manganese which developed in these tanks.

DISCUSSION

Observations of this biologically mediated transfer of dissolved to particulate manganese was not limited to this time period in the MERL tanks. This phenomena was observed on at least three previous occasions during the spring and summer in various tanks and during the early fall of 1977. Variability in bloom intensity and species composition complicates quantification of this phase transition in terms of geochemical cycling. It is quite evident, however, that certain organisms can dramatically alter the dissolved manganese concentrations of marine waters. It is not clear from the observed correspondence between particulate manganese and chlorophyll a if manganese is associating directly with the chlorophyll molecule or if the correspondence simply indicates that manganese is associating

TABLE 2

ESTIMATED RATIO OF MANGANESE TO CARBON IN PLANKTON*

Ratio of carbon to chlorophyll a, g/g	State of organism	Reference	Estimated Mn/C ratio,† 10^{-3} moles Mn/g C	Formation of particulate Mn in tank 2,‡ 10^{-6} moles $tank^{-1}$ day^{-1}
30 to 1	Vigorously growing	Parsons and Takahashi, 1973	1.1	900
50 to 1	Nutrient deficient	Parsons and Takahashi, 1973	0.66	500
280 to 1§	Growing	Vargo, 1978, MERL data for tank 2, August 1978	0.12	95
Unknown	Unknown	Hunt, 1979¶	0.09 ± 0.02	August¶
			0.02 ± 0.005	March¶

*Values were based on assumed and measured ratios of carbon to chlorophyll a and the influence of the ratio on estimates of manganese associated with organisms during growth.

†Molar ratio of manganese to chlorophyll a was taken to be 29 (Fig. 3), and the molecular weight of chlorophyll was taken to be 894 g.

‡Values were based on measured productivity of 330 mg C m^{-2} day^{-1} in tank 2 during August 1978.

§Ratio is at the lower end (285—1000) for starved cells (Sakshaug, 1977).

¶Plankton from Long Island Sound were sampled with a 20-mesh net in 1976. The plankton assemblage was dominated by the diatoms *Skeletonema c.* and *Chaetoceros* sp.

with the diatoms independently of the pigment and that the pigments happen to be a good measure of the surface on which this association occurs.

Mass-Balance Considerations

The importance of the observed transformation and deposition of dissolved to particulate manganese in the geochemical cycle of manganese was evaluated by a simple input—output model in the MERL tanks. The manganese flux through various compartments of the tanks over this entire period was determined from the data collected weekly. These results were summed and then converted to an average daily flux per tank (Fig. 5). The input functions for these models include the feedwater and benthic manganese flux. The output functions are described by losses from the tank during the feed cycle and manganese deposited in the sediments.

Addition of manganese to the tanks during the feed cycle was the same because all received identical additions of Narragansett Bay water each day. The net gain or loss of manganese in the tanks during the feed cycle was obtained by comparing the input to the output. The total acid-leachable manganese added to the tanks by the feed cycle was estimated from the weekly 500-ml grab samples. The total input was calculated from the average acid-leachable manganese concentration obtained from any two consecutive feed-water grab samples multiplied by the water volume added for the period. The estimated total input of manganese to the tanks from July 25 to Sept. 19 was 4400 μmoles or 80 μmoles per tank per day.

Manganese exported from the tank during the feed cycle was obtained by averaging the total acid-leachable manganese in a tank for any two consecutive weeks and multiplying by the total water volume lost that week. Comparing manganese in the tank effluent to that in the input over the August—September period indicates that tank 2 acted as a sink for manganese and tank 8 exported manganese (Fig. 5).

The source of the manganese exported from tank 8 was explained by the benthic manganese flux (Fig. 5) into the water, which represents 90% of the average daily addition of manganese to the tank water column over this period. Only a small fraction (<15%) of the benthic flux was exported from the tank, however. In addition, the total manganese concentration in the tank was not greatly altered during this period [Fig. 2(d)]. Thus a large internal return flux of manganese acted to balance the benthic flux. The rate of this return flux must be very rapid, otherwise increases in the standing crop of manganese on the order of 55 nmoles liter^{-1} day^{-1}

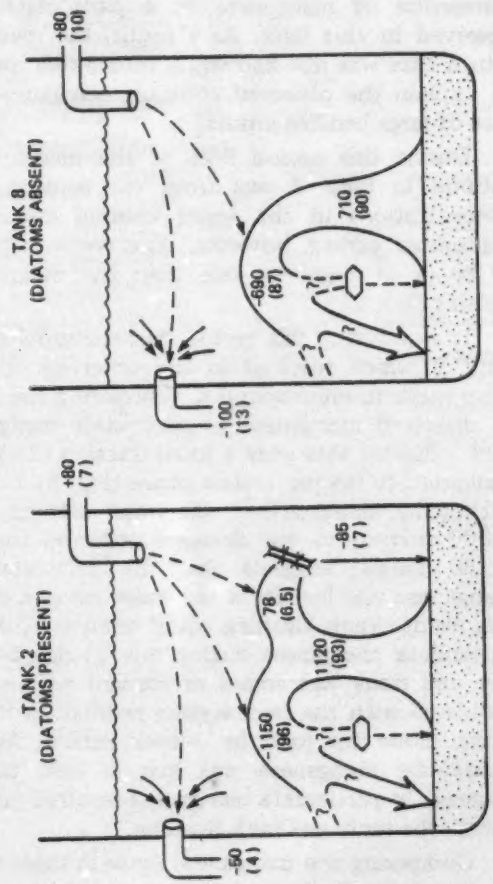

Fig. 5 Average daily manganese fluxes (μmoles Mn/tank/day) in MERL tanks 2 and 8, July—September 1978. Percentages of each flux compared with the total daily input of manganese into the tank water column (benthic flux plus feedwater additions) are shown in parentheses. Unknown pathways, which include wall adsorption, incorporation into resuspended sediment (⬡), and direct removal into the sediment surface, are broken lines.

would be observed within the tank. This clearly was not the case [Fig. 2(d)]. Increases in the standing crop of manganese in the MERL tanks from the benthic flux were not detected in other studies involving 4-hr sample periods. These results also support the presence of rapid return manganese flux in the tanks. Finally, conversion of manganese to a particulate state was not readily observed in this tank. As a result, the mechanism involved in the return flux was not known. A return flux must be present, however, to explain the observed constant manganese concentrations in the face of large benthic inputs.

During this period 93% of the manganese input to the water column in tank 2 was from the benthic flux. Total manganese concentrations in the water column declined over the August–September period, however. As a result, removal of manganese had to occur at a greater rate than the measured addition from the benthic flux.

It was during this period that the growth of diatoms occurred in tank 2 which resulted in the observed correlation of particulate manganese to chlorophyll a. Comparing the average daily conversion of dissolved manganese to particulate manganese with the benthic flux indicates that only a small fraction (7%) of the benthic flux was converted to the particulate phase (Fig. 5). Comparing the increase in particulate manganese in the water column from July 1 to Aug. 29 (2900 μmoles) to the decrease observed from Aug. 29 to Sept. 19 (2180 μmoles) suggests that the particulate phase carrying the manganese was lost from the water column during the later weeks of this event. Tank flushing could remove $\leq$50% of the newly formed particulate manganese during this 21-day period if 3% was lost per day and none was added or formed within the tank. Intermittent problems with the feed system resulted in the tanks' operating in a batch mode for half the 3-week period. As a result $<25\%$ of the particulate manganese was lost in feed tank flushing. Thus the decrease in particulate manganese resulted primarily from deposition within the tank, not tank flushing.

Comparing the manganese cycle in these two tanks indicates that the dominant input of manganese at this time in both tanks was from sediment. The benthic flux was balanced by a return flux that was not measurable in tank 8. In tank 2 a small fraction (7% of the benthic flux) was converted to the particulate phase during the moderate increase in the diatom population in the tank (Fig. 5). The phases involved in the major fraction of the return flux could not be determined in tank 2. Present investigations involve assessment of uptake by walls and onto resuspended material.

Estimated Manganese Uptake by Plankton on the Basis of Productivity

The mass-balance estimates for the removal of manganese by the diatom growth were compared with an estimate of the manganese removed based on productivity. The molar ratio of manganese to chlorophyll a was determined to be 29 (Fig. 3). This was converted to moles of manganese per gram of carbon by using literature estimates of the ratio of carbon to chlorophyll a in plankton. In addition, the carbon-to-chlorophyll ratio was measured at this time in tank 2; it is apparent that these ratios may vary widely (Table 2). The carbon-to-chlorophyll ratio was then multiplied by the measured productivity over this period in tank 2 [330 ± 60 mg C m^{-2} day^{-1} (Vargo, 1978)] to obtain an estimate of the daily conversion of dissolved manganese to the particulate phase as a result of the diatom growth (Table 2).

The manganese-to-carbon ratio obtained from typical literature ratios of carbon to chlorophyll a leads to high estimates for the manganese concentration in the plankton in comparison with results based on measured manganese-to-carbon ratios (Table 2). The manganese-to-carbon ratio observed in MERL tank 2 is in excellent agreement with that found in diatom-dominated plankton assemblages from Long Island Sound (Hunt, 1979). It is apparent from these results that we must be careful not to overextend results based on assumed ratios of carbon to chlorophyll a.

Comparing the conversion of dissolved to particulate manganese estimated from the mass balance (78 μmoles/day) with that determined from productivity (95 μmoles/day) by using a carbon-to-chlorophyll ratio of 280 shows close agreement. Assumed low ratios of carbon to chlorophyll a result in high estimates of the conversion of manganese to the particulate phase in comparison with observed results.

If the carbon-to-chlorophyll ratio was assumed to be 30 rather than the observed 280, the majority of the benthic flux in tank 2 could be returned to the sediment by the diatom. If diatoms were the major phase involved in the return flux of manganese, however, the steady-state condition observed for tank 8 could not be explained.

CONCLUSIONS

An examination of the manganese cycle in selected MERL microcosms during August–September 1978 indicated conversion of dissolved manganese to particulate manganese by diatoms. This

conversion supplied a minor mechanism for manganese removal. The conversion of dissolved manganese to particulate forms resulted in a dramatic decline in dissolved manganese. The dominant input of manganese to the water column of the MERL tanks was from the sediments. This input was balanced by a return flux that apparently operates on very rapid time scales. The mechanism and additional phases involved in this return flux have not been fully explained.

The observed diatom-mediated conversion of dissolved manganese to particulate manganese probably occurs in open estuaries. Observation of this conversion and the ability to determine its importance in the geochemical cycle of manganese is difficult in nature because of many factors, including physical mixing, freshwater inputs, and natural variability within estuaries. The results of this study demonstrate the ability of MERL microcosms, which maintain a reasonable analogue of a natural estuarine system and can be easily and repeatedly sampled, to provide basic data on the functioning of estuarine systems. More importantly, this facility provides the control necessary to measure various elemental fluxes through the system and to model them with a reasonable degree of confidence.

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